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Genetic algorithm prediction of crystal structure of metastable Si-IX phase

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ABSTRACT

We performed genetic algorithm search for the atomic structure of the long time unsolved Si-IX phase. We found two new structures with space groups of $P4_2/m$ and P-4, respectively, which have lattice parameters in excellent agreement with the experimental data. The phonon calculations showed that the $P4_2/m$ structure exhibits a soft phonon mode, while the P-4 structure is dynamically stable. Our calculation also showed that the P-4 structure is a meta-stable structure in a pressure range from 0 to 40 GPa. The Si-IX phase could be a mixed phase consisting of the $P4_2/m$ and the P-4 structures.

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Silicon is well-known for having various meta-stable phases at ambient condition as well as at high pressure. By compressing Si to high pressure, several high pressure phases such as β-Sn, Imma, simple hexagonal, Cmca, hexagonal closed-package or face-centered cubic phases were observed [1]. By either rapid or slow depressurization from high pressure, the Si high pressure phases can end up with some meta-stable phases at ambient condition such as st12, Si-VIII, Si-IX or Si-III [1,2]. Some other meta-stable phases such as Cmmm, body-centered tetragonal or $P6_122$ have also been found [18]. Atomic structures of all high pressure and meta-stable phases are known except those of Si-VIII and Si-IX phases. These two phases were observed in experiment by rapid depressurization Si from 14.8 GPa for Si-VIII and from 12 GPa or 13 GPa for Si-IX [2]. Moreover, Goswami et al. [20] reported Si-IX nano particles with size of 4–5 nm synthesized by thermal spraying. However, the detail atomic structures have not been solved for more than 2 decades, although X-ray diffraction data from experiment suggested tetragonal lattices for both Si-VIII and Si-IX phases [2].

In this paper, we performed crystal structure search using genetic algorithm to determine the crystal structure for Si-IX phase. Two candidate structures were found with excellent agreement in lattice parameters with the experimental values. We also show the results of an attempt to search for atomic structure of bigger unit cell Si-VIII phase.

The genetic algorithm (GA) atomic structure prediction was performed using real space cut and paste approach [3,4]. A fixed tetragonal unit cell with $a = 7.531$ Å and $c = 3.879$ Å according to experiment [2] was used. The number of Si atoms in the unit cell is determined to be 12 by comparing the density of Si-IX phase with that of Si-III phase [2]. The initial atomic positions of the 12 Si atoms were randomly generated. We used the structure pool size of 64 structures and in each generation 25% of structures in the pool were updated. We used different interatomic potentials to perform independent searches. These potentials are Tersoff [6], Stillinger–Weber [7] and Modified Embedding Atomic Model [8] potentials. The local structure relaxations during the GA searches were performed by LAMMPS code [9]. The low energy structures from each independent search were then collected and refined by first-principles density functional theory (DFT) calculations [5].

The DFT calculations were performed by VASP code [10] with PAW pseudopotential method [11,12] and generalized-gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [13] for the exchange-correlation functional. The energy cutoff was 320 eV and the Monkhorst–Pack's scheme [14] was used for Brillouin zone sampling. A high-quality k-point grid, which is corresponding to $7 \times 7 \times 7$ for Si diamond structure, was used in all calculations. In order to investigate the dynamical stability of the obtained structures, we used finite displacement method [15] to calculate the phonon frequencies throughout the Brillouin zone by VASP and Phonopy codes [16].

Before performing the search for the Si-IX phase, we validated the quality of the potentials used in our GA search by performing the "from-scratch" search for the ground state structure of Si with

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2–16 atoms per unit cell. The only given information to the GA searches was the number of atoms per unit cell. The lattice parameters and initial atomic positions were generated randomly. In these searches we recovered the ground state Si diamond structure as well as many low energy meta-stable structures of Si such as hexagonal diamond, body-centered tetragonal, Imma, Cmmm or P6$_1$22 structures [1,17,18]. These validation results suggest that the interatomic potentials would be suitable to use in our GA search for the metastable Si-IX phase.

We obtained two candidate structures for the Si-IX phase from our GA search. After full refinement by DFT calculations, the first structure has the symmetry of space group P4$_2$/m (#84) and lattice parameters $a=7.501$ Å and $c=3.902$ Å, which are very close to experimental values of 7.531 Å and 3.879 Å, respectively [2]. The 12 Si atoms occupy 3 4j Wyckoff positions: (-0.052445, 0.15957, 0.0), (0.77276, 0.68201, 0.0) and (0.49473, 0.83845, 0.0), respectively. The second structure has the symmetry of space group P-4 (#81) and lattice parameters $a=7.533$ Å and $c=3.918$ Å, which are also close to the experimental results [2]. The 12 Si atoms occupy 3 4h Wyckoff positions: (-0.06217, 0.21528, 0.00030), (0.38750, 0.1110, 0.49723) and (0.42326, -0.35228, 0.23739), respectively. The symmetries of these two structures are also very close to that of experimental proposed symmetry. However, the energies of these two structures are high, which are 0.338 eV/atom and 0.350 eV/atom higher with respect to that of the ground-state Si diamond structure. The atomic structures of these two structures are shown in Fig. 1. It is interesting to note that the 8 Si atoms from the last 2 Wyckoff positions of the P4$_2$/m structure make a Si nanotube at the center of the unit cell. This Si nanotube is the same as that in the recently proposed Cmmm structure [21]. The other 4 Si atom of the P4$_2$/m structure are at the corners of the unit cell binding the nanotubes together. We use different color (size) dots to distinguish the nanotube from the corner atoms of the P4$_2$/m structure in Fig. 1a. The unit cell of the P4$_2$/m structure in Fig. 1a is repeated twice along c direction to show the Si nanotube clearer. Beside these two structures, the orthorhombic Ibam structure [19], which was reported recently in an attempt to resolve the atomic structure of Si-IX phase, was also obtained from our GA search. Although the Ibam structure has lower energy than the P4$_2$/m and P-4 structures (0.204 eV/atom higher than the Si diamond structure), the lattice parameters do not match with the experimental values.

In order to check the stability of these two new structures, we calculated the phonon frequencies throughout the Brillouin zone by finite displacement method. While the phonon band structure of the P4$_2$/m structure shows soft modes, the phonon band structure of the P-4 structure does not show any negative phonon frequencies (Fig. 2). This means that the P4$_2$/m structure is dynamically unstable and the P-4 structure is dynamically stable. The bulk modulus of the P-4 structure is 77.12 GPa from our GGA-DFT calculation (the bulk modulus of the Si diamond structure is 90.19 GPa in the same parameters setting calculation). We also performed enthalpy calculation for the P-4 structure in the pressure range from 0 to 40 GPa to see whether we can stabilize this structure by pressurizing. The enthalpy of the P-4 structure is always higher than that of the Si diamond structure at any pressure in this pressure range, showing that the P-4 structure is a meta-stable structure in this pressure range.

The simulated X-ray diffractions of both the P42/m and P-4 structures recover most of the experimental X-ray diffraction peaks for Si-IX phase [2] with some differences in intensities. There are some extra peaks in the simulated spectra in comparison with the reported experimental data in Ref. [2]. Since the reported experimental data are not in enough detail to allow further analysis (e.g., Rietveld analysis), it is difficult to verify our newly found structures for the Si-IX phase at this point. Nevertheless, as discussed above, the lattice parameters of the dynamically unstable P4$_2$/m structure and those of the meta-stable P-4 structure are in excellent agreement with the lattice parameters obtained in experiment for the sample relaxed for 23 h and 14 days, respectively, after depressurization [2]. We believe that the Si-IX phase observed in experiment could be a mixed phase consisting of the P4$_2$/m and P-4 structures. More experiments may be needed to verify the prediction from the GA search.

We also did similar search for Si-VIII phase with the unit cell fixed to the experimental values: tetragonal unit cell with $a=8.627$ Å, $c=7.500$ Å and containing 30 Si atoms. However, after full DFT relaxation and symmetrization, we did not obtain any tetragonal structure with unit cell close to the experimental unit cell. We
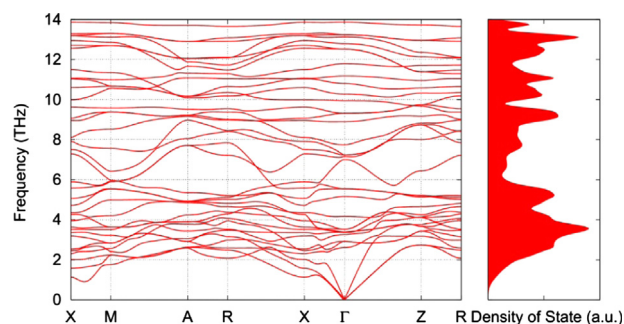

Fig. 2. (Colour online) The phonon band structure (left) and the phonon density of state (right) of the Si P-4 structure.
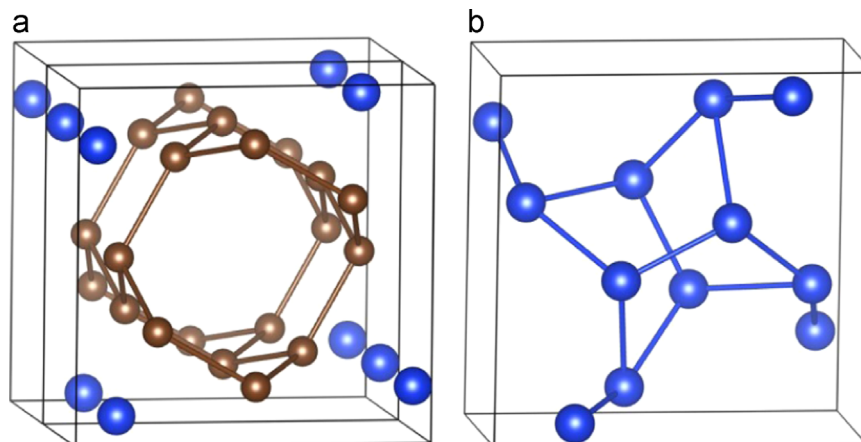

Fig. 1. (Colour online) Atomic structure of (a) Si P4$_2$/m and (b) Si P-4 structures. The unit cells are shown by solid lines and the dots are Si atoms.

obtained one structure with unit cell close to the experimental unit cell but the symmetry of that structure is quite different from the experiment observation. The lattice parameters of that structure are $a=8.735$ Å, $b=8.735$ Å, $c=7.705$ Å, $\alpha=90^{\circ}$, $\beta=90^{\circ}$ and $\gamma=90^{\circ}$ with the symmetry of space group Pm (#6). The formation energy of this structure is 0.27 eV/atom higher than that of Si diamond structure. More searches need to be done to find structures with better agreement with experiment for Si-VIII phase.

In conclusion, we found two candidate structures for the meta-stable Si-IX phase with excellent agreement in the lattice parameters with the experiment. The $P4_2/m$ structure is a dynamically unstable structure and P-4 structure is a meta-stable structure. The simulated X-ray diffractions from both structures show some agreement with the experimental data. However, more experimental data are needed to do further analyses to identify the Si-IX phase. We believe that Si-IX phase could be a mixed phase consisting of $P4_2/m$ and P-4 structures. We also found a Pm structure with lattice parameters close to the experimental values for Si-VIII phase, but the symmetry of this structure is quite different from the experiment observation. More searches need to be done to find an atomic structure with better agreement with experiment for Si-VIII phase.

Acknowledgments

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